PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C11D 17/00, 10/04, 3/386 // 1:14, 1:16, 1:22

A1

(11) International Publication Number: WO 98/54285

(43) International Publication Date: 3 December 1998 (03.12.98)

(21) International Application Number: PCT/US97/09265

(22) International Filing Date: 30 May 1997 (30.05.97)

(71) Applicant (*for all designated States except US*): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): FAKOUKAKIS, Emanuel, Pantelis [US/PH]; 1386 Palm Avenue, Dasmarinas Village, Makati, Metro Manila 1222 (PH). DY, Aimee, Go [PH/JP]; West Court 3 #2901, 5-11-501, Koyo-cho Naka, Higashinada-ku, Kobe 658 (JP). SHETH, Uday, Narendra [US/PH]; 1529 Carissa Street, Dasmarinas Village, Makati, Metro Manila 1222 (PH).

(74) Agents: REED, T. David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: LAUNDRY BAR WITH IMPROVED PROTEASE STABILITY

(57) Abstract

The invention relates to a built, high-moisture protease-containing laundry detergent bar with improved protease stability. The bars contain a stabilizing agent made of a borate compound in conjunction with either a polyol, a carboxylate salt, a carboxylic acid, or mixture thereof.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

LAUNDRY BAR WITH IMPROVED PROTEASE STABILITY

FIELD

The present invention relates to laundry bars, and more specifically to built laundry detergent bars containing protease enzymes and enzyme stabilizers.

BACKGROUND

In societies where mechanical washing machines are not common, laundry detergent bars comprising soap and/or synthetic organic surfactants and detergency builders are used in the laundering of clothes. Technical developments in the field of laundry detergent bars have concerned formulating bars which are effective in cleaning clothes; which have acceptable sudsing characteristics in warm and cool water and in hard and soft water; which have acceptable in-use wear rates, hardness, durability, and feel; which have low smear; and which have a pleasing odor and appearance. Methods for making laundry detergent bars are also well known in the art. Prior art disclosing laundry bars and methods for making laundry bars include: U.S. Pat. 3,178,370, Okenfuss, issued April 13, 1965; and Philippine Pat. 13,778, Anderson, issued September 23, 1980.

Laundry bar compositions often contain enzymes as additives to improve cleaning performance. Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles, for the prevention of refugee dye transfer in laundering, and for fabric restoration. Typically, laundry bar compositions have contained enzymes such as proteases, cellulases, amylases and lipases, and mixtures thereof. See for example, PH 9809 to Vasquez, issued March 26, 1976; and EP 425214 A to Donker, published May 2, 1991.

High moisture laundry bars are desirable because they provide properties valued by consumers, such as a smooth texture and a favorable wear rate. Unfortunately, detergent bars and specifically laundry bars containing both

protease enzymes and a high moisture content have usually been characterized by low enzyme stability. Protease enzymes are not suitably stable in high moisture laundry bar compositions over time.

Protease-containing high moisture laundry detergent bars usually possess high levels of protease activity during and immediately after the production process. However, it has been observed that this protease activity drops significantly as time passes. Although not wanting to be limited by theory, it is believed that this low stability is due to autolysis and protease degradation in the bar. As protease activity drops, cleansing performance drops accordingly. This continuing decrease in protease activity leads to a limited shelf-life for these bars. It is therefore desired to maintain stability of the protease enzyme in the bar over time.

Based on the foregoing, there is a need for maintaining protease enzyme stability in high-moisture laundry bars over time. None of the existing art provides all of the advantages and benefits of the present invention.

SUMMARY

The present invention is directed towards a high-moisture soap-synthetic laundry detergent bar containing:

a. from about 45% to about 75% of a soap;

b. from about 1% to about 15% of an anionic synthetic detergent;

c. from about 0.0001% to about 0.01% of a protease;

d. from about 0.1% to about 33% of a stabilizing agent, where the stabilizing agent is made from:

   i. a borate compound; and

   ii. an ingredient selected from the group consisting of polyols, carboxylic acids, carboxylate salts, and mixtures thereof;

e. from about 1% to about 50% of a builder; and

f. other detersive compounds,

wherein the laundry detergent bar contains a moisture level from about 20% to about 40% by weight in the finished bar composition.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure. All documents referenced herein are incorporated by reference in their entireties.

DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the present invention will be better understood through a careful reading of the following description.

In this specification all percentages are by weight of the total composition unless specifically stated otherwise.

All ratios are weight ratios unless specifically stated otherwise.

All temperatures are expressed in degrees Celsius, molecular weights are in weight average, and the decimal is represented by the point (.), unless otherwise indicated.

"Alkali earth metals" as used herein refers to metals of Group IIA of the periodic table.

"Alkali metals" as used herein refers to metals of Group IA of the periodic table.

"Alkyl" as used herein refers to the alkyl portion of acyl groups.

"Cleaning effective amount" refers to any amount of protease capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like.

"Comprising" as used herein means that other steps and other ingredients which do not adversely affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of."

All documents referenced herein are incorporated by reference in their entireties; however, citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

In accordance with the present invention it has been found that a built laundry detergent bar comprising a protease enzyme can achieve significantly improved protease enzyme stability over time in a bar composition which includes an appropriate stabilizing agent. Without intending to be limited by theory, it is believed that when in bar form, these compounds continue to protect the enzymes from irreversible denaturation and autolysis. However, upon use in laundering fabrics and other clothing items, it is believed that these water soluble

components are easily discharged from their protective duties. Thus, when water releases these stabilizers from the enzymes, it is believed that the enzymes thereupon regain their catalytic activity and begin work upon their intended substrates.

Soap

The soap suitable for use herein includes the water soluble salts of the higher fatty acids. Soap can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Preferred soap examples are the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soaps.

Preferred soap raw materials for the subject invention bars are soaps made from mixtures of fatty acids from tallow and coconut oil. Typical mixtures have tallow:coconut fatty acid ratios of 85:15, 80:20, 75:25, 70:30, and 50:50; preferred ratios are about 80:20 to 65:35.

Preferred soap raw materials for the subject invention are neat soaps made by kettle (batch) or continuous saponification. Neat soaps typically comprise from about 65% to about 75%, preferably from about 67% to about 72%, alkali metal soap; from about 24% to about 34%, preferably from about 27% to about 32%, water; and minor amounts, preferably less than about 1% total, of residual materials and impurities, such as alkali metal chlorides, alkali metal hydroxides, alkali metal carbonates, glycerin, and free fatty acids. Another preferred soap raw material is soap noodles or flakes, which are typically neat soap which has been dried to a water content of from about 10% to about 20%. The other components above are proportionally concentrated.

Soap will usually be present in the range from about 45% to about 75%, preferably from about 50% to about 75%, most preferably from about 55% to about 65% soap by weight of the total bar.

Anionic Synthetic Detergent

The anionic synthetic detergent suitable for use herein include the water soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl

group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. Examples of this group of synthetic detergents are the sodium and potassium alkyl sulfates (AS), especially those obtained by sulfating the higher alcohols (C_{8-18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkyl benzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patent 2,220,099 to Guenther et al, issued November 5, 1940, and U.S. Patent 2,477,383 to Lewis, issued July 26, 1949. Especially valuable are the linear straight chain alkyl benzene sulfonates (LAS) in which the average number of carbon atoms in the alkyl group is between about 11 to 13. LAS and other carbon chain-based compounds herein are abbreviated according to the average alkyl group length. For example, LAS with an average chain length of 12 carbon atoms is abbreviated as C_{12} LAS, even though it contains a distribution of LAS molecules with alkyl groups of differing lengths. Thus, for example, C_{10-18} LAS, as used below, indicates that groups of LAS molecules with chain lengths averaging from 10 carbon atoms to those groups of LAS molecules with chain lengths averaging from 18 carbon atoms, inclusive, are preferred herein. The alkali metal salts, particularly the sodium salts of these surfactants are preferred.

Other examples of an anionic synthetic detergent suitable for use herein are the sodium alkyl glyceryl ether sulfonates (AES), especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms. Preparation of alkyl glyceryl ether sulfonates are described in detail in U.S. Patent 3,024,273 to Whyte et al., issued March 6, 1962.

In addition, a suitable anionic synthetic detergent also includes the water soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to about 20 carbon atoms in the fatty acid group and from about 1 to about 10 carbon atoms in the ester group; water soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to about 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water soluble salts of olefin and paraffin sulfonates containing from about 12 to about 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to

about 3 carbon atoms in the alkyl group and from about 8 to about 20 carbon atoms in the alkane moiety.

Preferred anionic synthetic detergent examples are C_{10-18} alkyl sulfates (AS), C_{10-18} linear alkyl benzene sulfonates (LAS), C_{10-14} alkyl glyceryl ether sulfonates (AES), and mixtures thereof. The amount of anionic detergent in the compositions herein is from about 1% to about 15%, preferably from about 2% to about 12% by weight of the final bar composition.

Protease

Suitable examples of a protease useful herein are alkaline proteases and the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in U.S. Patent 3,723,250 to Aunstrup et al., issued March 27, 1973. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A and Protease B as disclosed in EP 130,756 A to Bott, published January 9, 1985. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 9318140 A1 to Aaslyng et al., published September 16, 1993. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Hansen et al., published March 5, 1992. Other preferred proteases include those of WO 9510591 A1 to Baeck et al., published April 20, 1995. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 A1 to Gerber, published March 23, 1995. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Branner et al., published November 10, 1994. Also preferred is "Protease D" as described in A. Baeck, et al, "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, filed October 13, 1994, and C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having U.S. Serial No. 08/322,677, also filed October 13, 1994.

Proteases are normally incorporated herein at levels sufficient to provide a "cleaning-effective amount." Additionally, higher protease levels may be desirable in highly concentrated detergent formulations. The preferred active

protease content of the compositions herein will typically comprise from about 0.0001% to about 0.01%, more preferably from about 0.0001% to about 0.003% by weight of the total bar composition. The amount of protease described above is the amount of "pure, active protease" in the total bar composition; i.e. about 0.0001% to about 0.01% of a 100% active protease preparation. Because protease activity varies greatly according to the enzyme, its preparation, and treatment, describing an exact weight percentage of commercially available preparations is impractical.

Stabilizing Agent

The stabilizing agent useful herein is characterized as containing a borate compound and an ingredient selected from polyols, carboxylate salts, carboxylic acids, and mixtures thereof. The stabilizing agent will typically be between from about 0.1% to about 33% by weight of the total bar composition, preferably from about 0.7% to about 21%, and more preferably from about 1.25% to about 16% by weight of the total bar composition.

There are many examples of suitable borate compound useful herein. Water-soluble borate compounds such as boric acid are preferred, although other compounds such as borax, boric oxide, hydroborates, and other alkali metal borates (e.g., sodium ortho-, meta-, and pyroborates and sodium pentaborate) are suitable. Substituted boric acids such as phenylboronic acid, butane-boronic acid, and p-bromo phenylboronic acid can also be used herein. Mixtures of the above borate compounds are also suitable for use herein. Typically, the borate compound will be between about 0.1% and about 10%, preferably from about 0.5% to about 5%, and more preferably from about 0.75% to about 4% by weight of the final bar composition. In relation to the amount of protease, the weight ratio of borate compound to protease useful herein is from about 100,000:1 to about 10:1 preferably between about 5,000:1 to about 167:1, and more preferably from about 1,000:1 to about 250:1.

Polyols useful in the present invention are characterized by solubility in water, carbon backbones of length between C_2 and C_6, and multiple hydroxyl groups, preferably containing between about 2 and about 6 hydroxyl groups per molecule. A useful description of the relationship between the amount of borate compound and the polyol level is found by utilizing a "borate ion:hydroxyl ratio." This ratio refers to the average molar ratio of borate ions $(B_4O_7)^{2-}$ to total number of hydroxyl groups from a polyol. For example, the borate ion:hydroxyl

ratio for one mole of sodium borate ($Na_2B_4O_7$) to one mole of 1,3-propane diol ($CH_2(OH)CH_2CH_2(OH)$) would be 1:2. The borate ion:hydroxyl ratio for one mole of sodium borate ($Na_2B_4O_7$) to one mole of glycerol ($C_3H_5(OH)_3$) would be 1:3. The borate ion:hydroxyl ratio useful herein will usually be between about 1:2 and about 1:6, preferably between about 1:2 and about 1:3, and more preferably about 1:2.

Polyols useful herein include, but are not limited to 1,2-butane diol, 3-chloro-1,2-propane diol, ethylene glycol, 1,2-hexane diol, glycerol, mannose, propylene glycol, sorbitol, sucrose, and mixtures thereof. Preferred polyols include 1,2-propane diol, propylene glycol, and mixtures thereof. The polyol level will usually be between about 1% and about 15%, and preferably between about 1.5% and about 10%, and more preferably between about 2% and about 8% by weight of the final bar composition.

Carboxylic acids and carboxylate salts useful in the present invention include the acid forms of carboxylic acids and polycarboxylates, the alkali metal and other salt-forms thereof, and mixtures thereof. Non-limiting examples of carboxylic acids and carboxylate salts include water soluble forms of citrate, formate, malate, maleate, succinate, adipic acid, glutaric acid, and mixtures thereof. Also useful herein are mixtures such as SOKOLAN™ DCS by BASF Corp., which contains succinic, adipic and glutaric acids. Preferred carboxylic acids and carboxylate salts include water soluble citrate derivatives and salts, such as sodium citrate, and water soluble formate derivatives and salts, such as sodium formate. Carboxylic acids and/or carboxylate salts will usually be present at a level between about 0.05% and about 8%, preferably between about 0.2% and about 6%, and more preferably between about 0.5% and about 4% by weight of the final bar composition.

Builders

Builders suitable for use herein assist in controlling mineral hardness and/or in the removal of particulate soils. Inorganic as well as organic builders can be used. Builder levels can vary widely depending upon the end use of the composition and its desired physical form. The builder will typically comprise at least about 1% to about 50%, preferably from about 5% to about 30% by weight of the final bar composition. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or phosphate-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkaloammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used and are preferred. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates can also be used (see, for example, U.S. Patents 3,159,581 to Diehl, issued December 1, 1964; 3,213,030 to Diehl, issued October 19, 1965; 3,400,148 to Quimby, issued September 3, 1968; 3,422,021 to Roy, issued January 14, 1969; and 3,422,137 to Quimby, issued January 14, 1969).

Examples of carbonate builders are the alkali earth metal and alkali metal carbonates as disclosed in U.S. Patent 4,174,291 to Benjamin et al., issued November 13, 1979. Preferred carbonate builders include sodium carbonate and calcium carbonate.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the NaSKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE 3,417,649 A to Rieck, published November 14, 1985 and DE 3,742,043 A to Rieck et al., published June 22, 1989. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1} \cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein.

Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$M_z(zAlO_2)_y]\cdot xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. In addition to their use as part of the stabilizing agent, polycarboxylate builders can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. As used herein, "poly-carboxylate" refers to compounds having a plurality of carboxylate groups. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkaloammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al., U.S. Patent 3,635,830, issued January 18, 1972; see also "TMS/TDS" builders of U.S. Patent 4,663,071 issued to Bush et al., on May 5, 1987, and cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679 to Rapko, issued December 2, 1975; 3,835,163 to Rapko, issued September 10, 1974; 4,158,635 to Crutchfield et al., issued June 19, 1979; 4,120,874 to Crutchfield et al., issued October 17, 1978; and 4,102,903 to Crutchfield et al., issued July 25, 1978.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxy benzene-2,4,6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly the sodium salts), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984 to Bush, issued January 28, 1986. Useful succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 200,263 to Barrat et al., published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226 to Crutchfield et al, issued March 13, 1979, U.S. Patent 3,308,067 to Diehl, issued March 7, 1967, and U.S. Patent 3,723,322 to Diehl, issued March 27, 1973.

Moisture

Moisture enhances the mixing of the bar ingredients and provides the detergent bar with acceptable feel and other physical characteristics. Moisture can be introduced into the mixture by various methods, for example, by being included with the soap, such as with neat soap, being included with other ingredients, and/or as free water added to the bar formulation. Moisture herein can be present from about 20% to about 40% moisture, preferably from about 20% to about 30% moisture, more preferably from about 23% to about 27% by weight of the finished bar composition.

Other Detersive Compounds

The compositions herein can optionally include one or more other detersive compounds for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. The following represent non-limiting, illustrative examples of such optional compounds.

The bars can also contain other enzymes in addition to protease enzymes, e.g., mixtures of cellulase enzymes and other enzymes. If present, suitable enzymes include cellulases, cutinases, amylases, lipases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial and fungal amylases.

In addition to soap and anionic synthetic detergents, optional detergent surfactants can be included at a level up to about 30%, more preferably from about 0.5 to about 10%, by weight of the composition. The types of detergent surfactants that can be used as optional surfactants include cationic, nonionic, amphoteric and zwitterionic surfactants, and mixtures thereof. See U.S. Pat. No. 3,664,961 issued to Norris on May 23, 1972, and EP 550,652 to Fu and Scheibel, published on April 16, 1992.

Polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions. SRA's can include a variety of charged, e.g., anionic or even cationic species, see U.S. Patent 4,956,447, issued September 11, 1990 to Gosselink et al., as well as noncharged monomer units. Their structures may be linear, branched or even star-shaped. They may include capping moieties which are especially effective in controlling molecular weight or altering the physical or surface-active properties. Structures and charge distributions may be tailored for application to different fiber or textile types and for varied detergent or detergent additive products.

The detergent composition can optionally contain a polyamine soil release agent related to modified polyamines. See U.S. Patent 5,565,145 issued October 15, 1996 to Watson et al.

Preferred polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

The preferred polyamine soil release agents that comprise the backbone of the compounds are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylenepentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372 to Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C_2 alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have

at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:

$$[H_2NCH_2CH_2]_n-[\overset{H}{\overset{|}{N}}CH_2CH_2]_m-[\overset{|}{N}CH_2CH_2]_n-NH_2$$

wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306 to Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746 to Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095 to Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839 to Crowther, issued September 17, 1957; and U.S. Patent 2,553,696 to Wilson, issued May 21, 1951.

The polyamine soil release agents of the present invention, if included in the detergent composition, are included from about 0.01% to about 5%; preferably about 0.3% to about 4%; more preferably about 0.5% to about 2.5%, by weight of the detergent composition.

A particularly preferred optional component of the present invention is a detergent chelant. Such chelants are able to sequester and chelate alkali cations (such as sodium, lithium and potassium), alkali earth metal cations (such as magnesium and calcium), and most importantly, heavy metal cations such as iron, copper, manganese, zinc and aluminum. Preferred cations include sodium, copper, magnesium, zinc, and mixtures thereof. The detergent chelant is particularly beneficial for maintaining good cleaning performance and improved surfactant mileage, despite the presence of the softening clay and clay flocculating agents.

When present, detergent chelants are preferably phosphonate chelants, particularly one selected from the group consisting of diethylenetriamine

penta(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof, and an acetate chelant, particularly one selected from the group consisting of diethylenetriamine penta(acetic acid), ethylene diamine tetra(acetic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate) diethylenetriamine penta (acetate), and mixtures thereof. Preferably such salts or complexes have a molar ratio of metal ion to chelant molecule of at least 1:1, preferably at least 2:1. The detergent chelant can be included in the laundry bar at a level up to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.2% to about 2%, and even more preferably from about 0.5% to about 1.0%.

Glycerine is commonly incorporated in laundry bar compositions. If included, it is typically at concentrations up to about 3%, preferably about 0.5-1.5%.

The detergent compositions herein may also optionally include dyes, colorants, perfumes, dye-transfer inhibitors, alkoxylated polycarbonates, suds suppressers, structurants, binders, bleaching compounds, bleaching activators, clay soil removal agents, anti-redeposition agents, polymeric dispersing agents, brighteners, fabric softeners, and/or other compounds known in the art.

Processing

The detergent laundry bars of the present invention can be processed in conventional soap or detergent bar making equipment with some or all of the following key equipment: blender/mixer, mill or refining plodder, two-stage vacuum plodder, logo printer/cutter, cooling tunnel and wrapper.

In a typical process the raw materials are mixed in the blender/mixer. An alkaline inorganic salt (preferably soda ash) and an inorganic filler are mixed in the blender/mixer. The anionic synthetic detergent, either in its acid or salt form, is added into the mixture to effect neutralization in the case of an acid, or to effect better mixing/blending in the case of a salt. Optional detergents can also be added at this point. Moisture can be added here to accelerate the neutralization in the case that the anionic synthetic detergent is added in its acid form. It is preferred that builders are added next. If desired, polyphosphate can be added and used as an alkaline salt in the neutralization. The mixing time at

this point could take from one minute to one hour, with the usual mixing time being between two to twenty minutes.

While it is possible to add the stabilizing agent at other times, it is preferred that the stabilizing agent be added to the mixture immediately prior to the addition of protease. Thus, it is preferred that the stabilizing agent be added at the point, as well as some of the other detersive compounds; these can include, but are not limited to, the following: brightener, colorant, structurant, binder, photoactive bleach, soil release polymer, and anti-redeposition agent. It is preferred that the protease and any other enzymes then be added. Soap is then added, followed by additional mixing to homogenize the batch. The mixing time can take from one minute to an hour, with the usual mixing time being from two to twenty minutes. Any remaining optional other detersive compounds are then added, followed by an additional amount of filler that helps to harden up the otherwise fluid or doughy batch. Perfume is added towards the end of the blending to prevent losing it via volatilization. The blender mix is then charged to a surge tank. The product is conveyed from the surge tank to the mill via a multi-screw conveyer.

After milling or preliminary plodding, the product is then conveyed to a two-stage vacuum plodder, operating at high vacuum, e.g. 600 to 740 mm of mercury vacuum, so that entrapped air/gas is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar can be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

Examples of the invention are set forth hereinafter by way of the following non-limiting aspects and embodiments. It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from the scope of the present invention. The aspects and embodiments of the present invention set forth in this document have many surprising advantages, including significantly increased protease enzyme stability.

Examples 1-8

Ingredients	1	2	3	4	5	6	7	8
LAS	2.50	2.50	2.48	2.50	2.50	2.50	2.30	2.36
Soap* (80TLO/20CNO)	47.50	47.50	47.03	47.50	47.50	47.50	43.70	44.89
Savinase® 4T**	0.10	0.10	0.10	0.08	0.08	0.08	0.12	0.12
Boric Acid	2.00	4.00				3.00	4.00	
Borax			6.00	2.00	4.00			4.00
Sodium formate				2.00				
Sodium citrate	4.00	4.00	3.30		4.00	3.30	3.30	4.00
Sodium carbonate	3.00	8.00	6.00	3.00	8.00	6.00	3.00	8.00
Glycerol		2.00	5.00					
Propylene glycol	8.00	4.00	2.00	2.00	4.00	6.00	5.00	4.00
Ethylene glycol					2.00			
MgSO4	2.00		1.98		2.00		1.84	
Soda Ash	3.00	3.00	2.97	3.00	8.00	8.00	7.49	7.68
STPP	5.00	5.00	4.95	5.00	5.00	5.00	4.60	4.73
Talc	6.06	8.06		1.06	1.06	3.06		
Moisture	23.00	23.00	29.97	30.00	23.00	23.00	30.00	30.00
Other Detersive Compounds***	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

* soap composition is 80% Tallow and 20% Coconut

** SAVINASE® 4T is a commercial enzyme preparation from Novo which contains about 1% active protease.

*** brighteners, perfume, etc.

All amounts in the above table are measured as percentages of the total finished bar composition.

Example 9

A laundry detergent bar as described in the formulation of Example 1 is made, containing 0.10% by weight of SAVINASE® 4T by Novo, corresponding to an activity level of about 0.001 AU per gram. Boric acid and sodium citrate are added so as to amount to 2% and 4% of the finished product, respectively. Propylene glycol is added so as to total 8% of the finished product. Other detersive compounds are also added.

The bars are made by the process described above.

WHAT IS CLAIMED IS:

1. A laundry detergent bar comprising:
   a. from about 45% to about 75% of a soap;
   b. from about 1% to about 15% of an anionic synthetic detergent;
   c. from about 0.0001% to about 0.01% of a protease;
   d. from about 0.1% to about 33% of a stabilizing agent, said stabilizing agent comprising:
      i. a borate compound; and
      ii. an ingredient selected from the group consisting of polyols, carboxylic acids, carboxylate salts, and mixtures thereof;
   e. from about 1% to about 50% of a builder; and
   f. other detersive compounds,

   wherein said laundry detergent bar contains a moisture level from about 20% to about 40% by weight in the finished bar composition.
2. A laundry detergent bar according to Claim 1, wherein said soap is selected from the group consisting of sodium and potassium salts of tallow soap, sodium and potassium salts of coconut soap, and mixtures thereof.
3. A laundry detergent bar according to Claim 1, wherein said anionic synthetic detergent is selected from the group consisting of C_{10-18} alkyl sulfates, C_{10-18} linear alkyl benzene sulfonates, C_{10-14} alkyl glyceryl ether sulfonates, and mixtures thereof.
4. A laundry detergent bar according to Claim 1, wherein said protease is selected from the group consisting of alkaline protease, subtilisins obtained from particular strains of *B. subtilis* and *B. licheniformis*, and mixtures thereof.
5. A laundry detergent bar according to Claim 1, wherein:

a. said borate compound is selected from the group consisting of alkali metal borates, borax, boric acid, boric oxide, hydroborates, substituted boric acids, and mixtures thereof; and

b. said ingredient is selected from the group consisting of 1,2-butane diol, 3-chloro-1,2-propane diol, ethylene glycol, 1,2-hexane diol, glycerol, mannose, 1,2-propane diol, propylene glycol, sorbitol, sucrose, water soluble citrate derivatives and salts, water soluble formate derivatives and salts, water soluble malate derivatives and salts, water soluble maleate derivatives and salts, water soluble succinate derivatives and salts, water soluble adipic acid derivatives and salts, water soluble glutaric acid derivatives and salts, and mixtures thereof.

6. A laundry detergent bar according to Claim 1, wherein said borate compound and said protease have a ratio of from about 100,000:1 to about 10:1 by weight.

7. A laundry detergent bar according to Claim 1, wherein said borate compound and said polyol have a borate ion:hydroxyl ratio from about 1:2 to about 1:6.

8. A laundry detergent bar according to Claim 1, wherein said builder is selected from the group consisting of sodium tripolyphosphates, tetra sodium pyrophosphates, glassy polymeric meta-phosphates, orthophosphates, zeolites, polycarboxylates, and mixtures thereof.

9. A laundry detergent bar comprising:

a. from about 50% to about 75% of a soap selected from the group consisting of sodium and potassium salts of tallow soap, sodium and potassium salts of coconut soap, and mixtures thereof;

b. from about 2% to about 12% of an anionic synthetic detergent selected from the group consisting of C_{10-18} alkyl sulfates, C_{10-18} linear alkyl benzene sulfonates, C_{10-14} alkyl glyceryl ether sulfonates, and mixtures thereof;

c. from about 0.0001% to about 0.01% of a protease selected from the group consisting of alkaline protease, subtilisins obtained from particular strains of *B. subtilis* and *B. licheniformis*, and mixtures thereof;

d. from about 0.1% to about 33% of a stabilizing agent, said stabilizing agent comprising:

i. a borate compound selected from the group consisting of alkali metal borates, borax, boric acid, boric oxide, hydroborates, substituted boric acids, and mixtures thereof; and

ii. an ingredient selected from the group consisting of 1,2-butane diol, 3-chloro-1,2-propane diol, ethylene glycol, 1,2-hexane diol, glycerol, mannose, 1,2-propane diol, propylene glycol, sorbitol, sucrose, water soluble citrate derivatives and salts, water soluble formate derivatives and salts, water soluble malate derivatives and salts, water soluble maleate derivatives and salts, water soluble succinate derivatives and salts, water soluble adipic acid derivatives and salts, water soluble glutaric acid derivatives and salts, and mixtures thereof;

e. from about 1% to about 50% of a builder selected from the group consisting of sodium tripolyphosphates, tetra sodium pyrophosphates, glassy polymeric meta-phosphates,

orthophosphates, zeolites, polycarboxylates, and mixtures thereof; and

f. other detersive compounds,

wherein said laundry detergent bar contains a moisture level from about 20% to about 40% by weight in the finished bar composition.

10. A laundry detergent bar according to Claim 9, wherein said borate compound and said protease have a ratio of from about 100,000:1 to about 10:1 by weight.

11. A laundry detergent bar according to Claim 9, wherein said borate compound and said polyol have a borate ion:hydroxyl ratio from about 1:2 to about 1:6.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/09265

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D10/04 C11D3/386 //C11D1:14,C11D1:16, C11D1:22

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	GB 2 271 120 A (UNILEVER PLC.) 6 April 1994 see the whole document ---	1-8
A	WO 96 35772 A (THE PROCTER & GAMBLE CO.) 14 November 1996 see page 7, line 22 - line 25; claim 1 ---	1-3,8,9
A	EP 0 425 214 A (UNILEVER PLC.) 2 May 1991 cited in the application see column 4, line 26 - column 6, line 53 see claim 1; example 10 ---	1,2,4,5,8,9

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 January 1998	09/02/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serbetsoglou, A

1

INTERNATIONAL SEARCH REPORT

Interr ;al Application No
PCT/US 97/09265

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 798 181 A (VAZQUEZ S. M.) 19 March 1974 see column 3, line 21 - column 7, line 44 see claims & PH 9 809 A (COLGATE-PALMOLIVE CO.) 26 March 1976 cited in the application	1,3-5,8, 9
A	PH 13 778 A (THE PROCTER & GAMBLE CO.) 23 September 1980 cited in the application see page 8, line 10 - page 13, line 23 see page 19, line 10 - page 30, line 7 see claims 1-11	1-3,8
A	WO 95 27036 A (THE PROCTER & GAMBLE CO.) 12 October 1995 see page 10, line 24 - line 28 see claims 1-8; examples 11-15	1-4,8,9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/09265

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2271120 A	06-04-94	BR 9303954 A	03-05-94
		CN 1088611 A	29-06-94
		ZA 9307274 A	30-03-95
WO 9635772 A	14-11-96	NONE	
EP 0425214 A	02-05-91	CA 2028203 A	24-04-91
		JP 3185098 A	13-08-91
US 3798181 A	19-03-74	AR 198483 A	28-06-74
		CA 982506 A	27-01-76
PH 13778 A		NONE	
WO 9527036 A	12-10-95	CN 1145093 A	12-03-97
		CN 1145094 A	12-03-97
		CN 1145095 A	12-03-97
		WO 9527037 A	12-10-95
		WO 9527038 A	12-10-95